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NO DRAWINGS

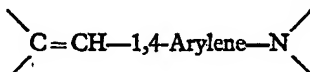
- (21) Application No. 37810/69 (22) Filed 28 July 1969
 (31) Convention Application No. 11234 (32) Filed 26 July 1968 in
 (33) Switzerland (CH)
 (45) Complete Specification published 5 July 1972
 (51) International Classification C09B 1/00
 (52) Index at acceptance
 C4P D1X Q4A3 Q4A5 Q4A7 Q4B10 Q4B11 Q4B12
 Q4B14 Q4B15 Q4B16 Q4B2 Q4B5 Q4B6
 Q4B8 Q4C



(54) ANTHRAQUINONE DYESTUFFS, THEIR PREPARATION AND THEIR USE

(71) We, CIBA-GEIGY A.G., formerly CIBA Limited, a Body Corporate organised according to the laws of Switzerland, of Basle, Switzerland, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

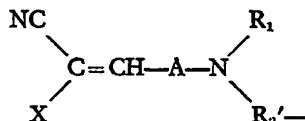
The present invention provides dyestuffs, which are free from sulphonic acid groups and in which the residue of an anthraquinonoid dyestuff is linked with at least one residue of a styryl dyestuff containing a styryl radical of the formula



in which the terminal carbon atom carries two organic residues.

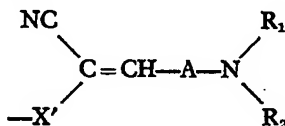
The residue of the styryl dyestuff can be linked to the anthraquinone nucleus in two ways, either *via* a negative group which is attached to the terminal carbon atom of the above styryl dyestuff radical, the negative group being e.g. a sulphonamido group or carboxylic acid group in which —SO₂ and —CO respectively are bound to the terminal carbon atom (cf. second formula below), or preferably, the styryl residue is linked to the anthraquinone nucleus *via* an alkyl group which is attached to the nitrogen atom of the above styryl radical and which may contain any desired substituents. A negative group or substituent has a positive sigma-value according to the HAMMETT equation (when attached in *p*-position at a benzene nucleus), the values being given e.g. in the text book of Heinz A. STAAB, Einführung in die theoretische organische chemie, 2nd Edition, Verlag Chemie, 1960, Weinheim/Bergstrasse, Germany, page 584.

Accordingly, preferred anthraquinone dyestuffs are those which contain a styryl residue of the formula



in which R₁ represents an unsubstituted or substituted alkyl group, R₂' represents an unsubstituted or substituted alkylene residue, A represents an unsubstituted or substituted para-phenylene residue and X represents a negative substituent, for example, a cyano, carbalkoxy, carbonamido or arylsulphonyl group.

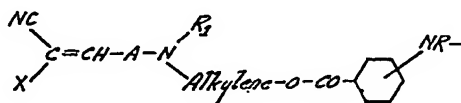
Another preferred type of the new dyestuffs are anthraquinone dyestuffs that contain a residue of the formula



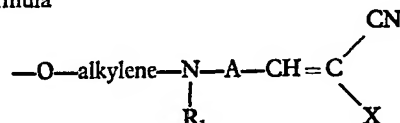
[Price 25p]

in which A and R₁ have the meanings given above, R₂ has the same meaning as R₁, and the residues R₁ and R₂ may be identical or different from each other, and X' represents a residue bound to the residue of the styryl dyestuff through an —SO₂— or —CO— bridge, being for example an —SO₂-arylene, —SO₂-N-(alkyl)-alkylene, —CO-N-(alkyl)-alkylene or —CO-O-alkylene residue, in which alkyl and alkylene represent unsubstituted or substituted alkyl, aralkyl or cycloalkyl groups.

Other dyestuffs of interest are those which contains a styryl residue of the formula



in which R represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms, and R₁, X and A have the same meanings as above, and those which contains a styryl residue of the formula



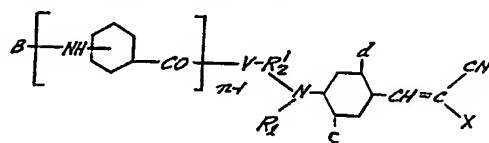
in which R₁, X and A have the same meanings as above.

The anthraquinonoid residues may be anthraquinone residues bound to the styryl dyestuffs (1) in an α-position or (2) in a β-position.

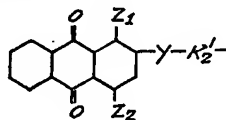
Anthraquinones substituted in α-position contain, for example, a substituted amino group or aminophenylamino group which carries the residue of a styryl dyestuff.

Anthraquinones substituted in β-position contain in the linking position, for example, a sulphonyloxy or carbonyloxy residue derived from the corresponding anthraquinonesulphonic or -carboxylic acid.

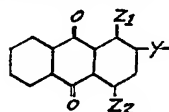
Valuable dyestuffs are those of the formula



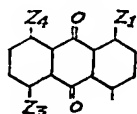
in which V represents —O— or —NH—, R₁ represents an unsubstituted or substituted alkyl group or a residue of the formula



wherein R₂' represents an unsubstituted or substituted alkylene group, Y represents an —SO₂— or preferably a —CO— group; n=1 or 2; c and d each represents a hydrogen or chlorine atom or a methyl, ethyl, methoxy or ethoxy, phenylthio or phenoxo group; X represents a carbalkoxy group, a carbonamide group, an arylsulphonyl or a cyano group, and B represents a residue of one of the formulae

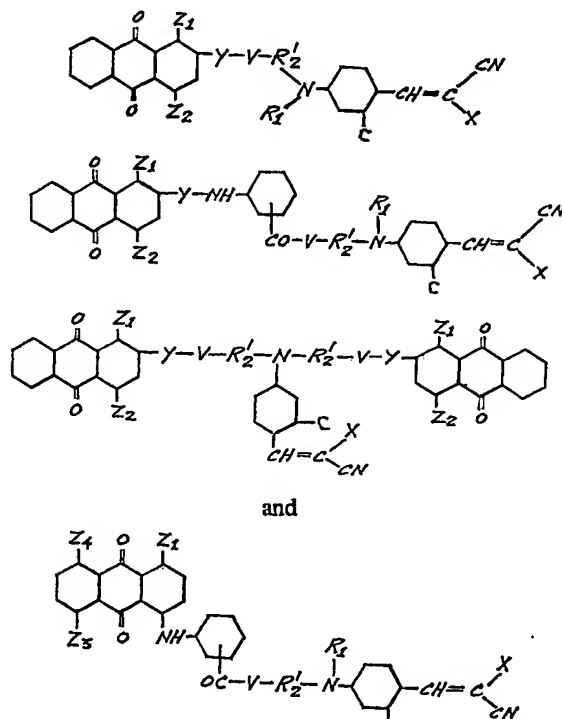


or

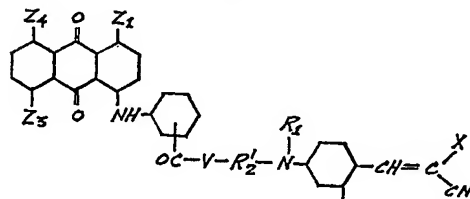


in which Z_1 is an amino group which may be alkylated, or a hydroxyl group, Z_2 represents an amino group which may be alkylated or a nitro group or a bromine atom, and Z_3 and Z_4 each represents a nitro or hydroxyl group or an amino group which may be alkylated.

Of special value are, for example, the dyestuffs of the formulae



and



The groups R_1 and R_2' each represent alkyl groups containing 1 to 4, preferably 2 to 4, carbon atoms, for example, methyl, ethyl, propyl or *n*-butyl groups which may be substituted in the usual manner, for example, aralkyl residues, for example, benzyl or β -phenethyl residues, halogenated alkyl groups, for example, β -chloroethyl, β,β,β -trifluoroethyl, β,γ -dichloropropyl, β -cyanoethyl, β -cyanoethoxyethyl, alkoxyalkyl, for example, β -methoxyethyl, β -ethoxyethyl or δ -methoxy-butyl, glycidyl, hydroxyalkyl, for example, β -hydroxyethyl, β,γ -dihydroxypropyl, nitroalkyl, for example, β -nitroethyl, carbalkoxy, for example β -carbo (methoxy, ethoxy or propoxy)-ethyl [in which the terminal alkyl group may carry in the ω -position cyano, carbalkoxy and acyloxy groups], β - or γ -carbo(methoxy or ethoxy)propyl, acylaminoalkyl, for example, β -(acetyl or formyl)-aminoethyl, acyloxyalkyl, for example, β -acetyloxyethyl, β -propionyloxyethyl, β -butyryloxyalkyl, β,γ -diacetoxypropyl, γ -acetylaminopropyl, γ -propionylaminopropyl, β -(alkyl or aryl)-sulphonylalkyl, for example, β -methanesulphonyl-ethyl, β -ethanesulphonyl-ethyl, β -(para-chlorobenzenesulphonyl)-ethyl, alkyl- or arylcarbamoyloxyalkyl, for example, β -methyl-carbamoyloxyethyl and β -phenylcarbamoyloxyethyl, alkyloxycarbonyl-oxyalkyl, for example, β -(methoxy, ethoxy or isopropoxy)-carbonyloxyethyl, γ -acetamidopropyl, β -(para-nitrophenoxy)-ethyl, β -(para-hydroxyphenoxy)-ethyl, β -(β' -acetyloxyethoxycarbonyl)-ethyl, β -[(β' -cyano-, hydroxy-, methoxy- or acetoxy)-ethoxycarbonyl]-ethyl, cyanoalkoxyalkyl, β -carboxyethyl, β -acetyloxyethyl, γ -aminopropyl, β -diethylaminoethyl, β -cyanoacetoxyethyl and β -benzoyl- or β -(para-alkoxy or phenoxy-benzoyl)-ethoxy groups.

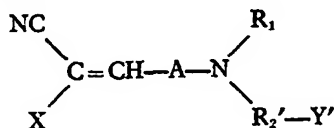
Generally, the group R_1 contains no more than 18 carbon atoms.

The group R_2' is an alkylene group containing 1 to 4 carbon atoms, which may contain one or more substituents, for example, hydroxyl or acyloxy groups.

The present invention also provides a process for preparing the above-mentioned dyestuffs, wherein at least one anthraquinone derivative is condensed according to known methods with at least one styryl dyestuff as above defined, and, if desired, acylated according to known methods with a fibre-reactive group containing acylating

agent. The word 'known' is to be understood as designating methods described in the literature on the subject.

Preferred reactants are those of which one contains a labile negative group and the other a substitutable nucleo-philic group, for example, a hydroxyl, mercapto or amino group. Thus, a starting styryl dyestuff may be used of the formula

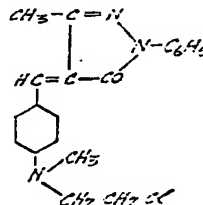
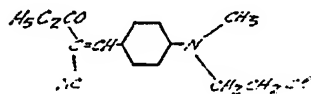
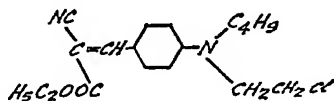


in which R_1 represents an unsubstituted or substituted alkyl group, R_2' represents an unsubstituted or substituted alkylene group, A represents an unsubstituted or substituted *p*-phenylene group, X represents a negative substituent and Y' represents a group which contains a labile hydroxyl or amino group. It is also possible to carry out other reactions on active double bonds.

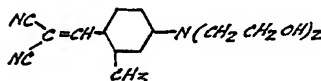
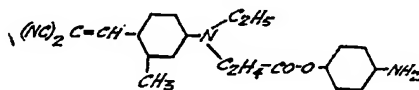
A fibre-reactive group, referred to above, is a labile group capable of forming a covalent link with a hydroxy or amino group in natural or man-made textile substrates in a neutral or preferably alkaline medium.

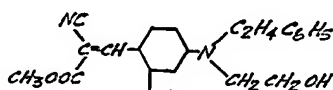
A. Starting compounds of the styryl series

(I) Reactive styryl dyestuffs that contain a labile negative residue, for example the styryl dyestuffs of the formulae

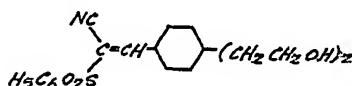


(II) Reactive styryl dyestuffs that contain a nucleophilic substitutable residue, for example, the dyestuffs of the formulae





and



The styryl dyestuffs can be prepared in the usual manner by way of the Vilsmeier reaction from a dialkylaniline and condensation of the intermediately formed γ -formylaniline with a methylene-active compound.

Methylene-active compounds of the formula $\text{NC}-\text{CH}_2-\text{X}$ suitable for the reaction are, for example:

malonic acid dinitrile,
cyanoacetic acid methyl ester, ethyl ester and butyl ester,
cyanoacetamide,
cyanoaceto dimethylamide and methylamide,
methylsulphonyl acetonitrile,
phenylsulphonyl acetonitrile and
para-toluylsulphonyl acetonitrile.

B. Starting compounds of the anthraquinone series

(I) Starting compounds that contain a negative group which is labile (i.e. can be eliminated)

1. Anthraquinone compounds that contain a negative mobile substituent in the α -position, for example:

1-halogenanthraquinones, preferably 1-bromo- or 1-chloro-anthraquinones, for example,
1-bromo-4-methoxyanthraquinone,
1-bromo-3-phenyloxy-4-aminoanthraquinone,
1-amino-4-bromo-anthraquinone-2-carboxylic acid-N,N-dimethylamide,
1-amino-4-chloro-2-methoxycarbonyl-anthraquinone,
1-amino-4-bromo-2-methoxycarbonyl-anthraquinone,

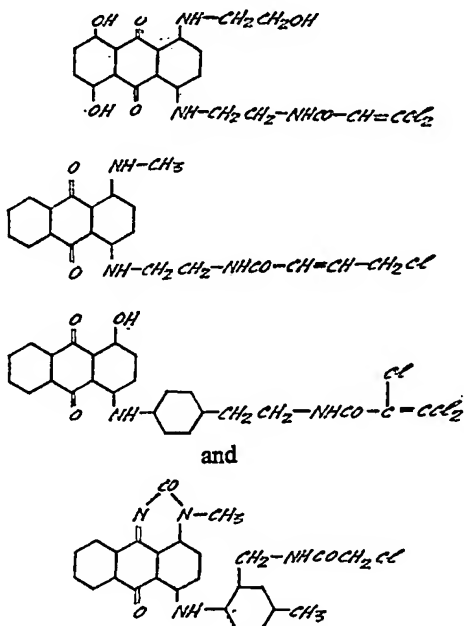
as well as anthraquinones that contain active halogen atoms, for example:

1-hydroxy-4-(3-chlorocarbonylphenyl)-aminoanthraquinone and
1-amino-2-bromo-4-(3'-nitro-4'-chlorophenylsulphonyl) - amino - anthraquinone.

Another group of starting materials comprises the 1-nitro-anthraquinones which can be reacted with a styryl dyestuff containing a primary amino group by a method known *per se*, with replacement of the nitro group by the amino group, for example, 1,5-dihydroxy-4,8-dinitro-anthraquinone. Moreover, there should be mentioned in this connection those α -hydroxyanthraquinones which in the presence of a reducing agent exchange hydroxyl groups for amino residues, especially 1,4-dihydroxyanthraquinone whose hydroxyl groups can be considered to be negative residues for the present purpose.

Furthermore, there should be mentioned anthraquinone derivatives that contain in α -position one or several fibre-reactive groups, for example:

1-[4'-(4''-chloro-6''-methoxy-1'',3'',5''-triazinyl-2''-amino)-anilino]-anthraquinone,
1,4-bis-(γ -chloro- β -hydroxy-propylamino)-anthraquinone,
1- β -hydroxyethylamino-4-(γ -chloro- β -hydroxypropylamino)-anthraquinone,
1-methylamino-4-(γ -chloro- β -hydroxy-propyl)-amino-anthraquinone,
1-(γ -chloro- β -hydroxypropyl)-amino-4-(4'-methylcyclohexylamino)-anthraquinone,
1-methylamino-4-[2'-chloro - 4' - bis-(hydroxyethyl)-amino-1',3',5'-triazinylamino]-anthraquinone,
1-methylamino-4-(2'-bromomethylamino)-anthraquinone,
1,4-bis-(γ -bromopropylamino)-anthraquinone,
1-amino-4-(3'-chloroacetyl-anilino)-anthraquinone,
and the dyestuffs of the formulae



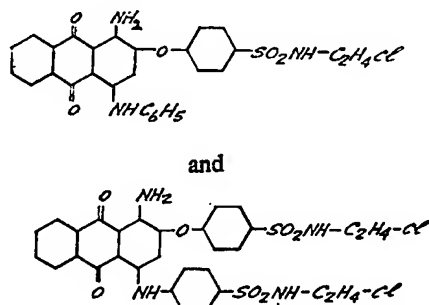
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2. Anthraquinonoid starting dyestuffs containing labile negative groups, linked in the β -position, are the following compounds:
- 1-amino-4-nitroanthraquinone-2-carboxylic acid chloride,
- 1-amino-4-(4'-carbonamidophenyl)-aminoanthraquinone-2-carboxylic acid chloride,
- 1,4-dihydroxy-2-chloromethylphenylmercapto-anthraquinone,
- as well as the compounds of the formulae

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- (II) Anthraquinone dyestuffs containing nucleophilic substitutable groups are, for example:

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- 1-amino- and 2-amino-anthraquinone,
- 1-amino-5-chloro-8-hydroxyanthraquinone,
- 1-amino-2-bromo-anthraquinone,
- 1-amino-5-hydroxy-6,8-dichloro-anthraquinone,
- 1-amino-5,8-dichloro-anthraquinone,
- 1-amino-5-nitro-anthraquinone,
- 1-amino-5-chloro-8-methoxy-anthraquinone,
- 1-amino-7-chloro-anthraquinone,
- 1-amino-6-chloro-anthraquinone,
- 1-amino-6- or 7-fluoro-anthraquinone,
- 1-amino-6- or 7-bromo-anthraquinone,
- 1-amino-6,7-dichloro-anthraquinone,
- 1-amino-6,7-difluoro-anthraquinone,
- 1-amino-2-(β -hydroxyethoxy)-4-hydroxy-anthraquinone,
- 1-amino-2-bromo-anthraquinone,
- 1-amino-2-methyl-anthraquinone,

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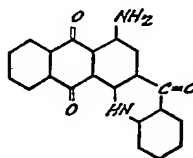
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	1-(β -aminoethylamino)-4-acetylamino-anthraquinone,	
	1-(β -aminoethylamino)-anthraquinone,	
	1-acetylamino-4-hydroxy-anthraquinone,	
5	1-amino-4-hydroxy-anthraquinone,	5
	1-amino-4-chloro-anthraquinone,	
	1-amino-4-guanidino-anthraquinone,	
	1-amino-4-(β -hydroxyethylamino)-anthraquinone,	
	1-amino-2,4-dibromo-anthraquinone,	
10	1-(2-hydroxyethylamino)-anthraquinone,	10
	1-amino-2-isopropylmercapto-anthraquinone,	
	1-amino-2-methoxy-4-hydroxy-anthraquinone,	
	1,2-diamino-anthraquinone,	
	1-hydroxy-anthraquinone,	
	2-hydroxy-anthraquinone,	
15	1,2-dihydroxy-anthraquinone,	15
	1,4-dihydroxy-anthraquinone,	
	1,8-dihydroxy-anthraquinone,	
	1,2,4-trihydroxy-anthraquinone,	
	2,6-dihydroxy-anthraquinone,	
20	1,2,5,8-tetrahydroxy-anthraquinone,	20
	1,2,4,5,6,8-hexahydroxy-anthraquinone,	
	1-hydroxy-4-acetylamino-anthraquinone,	
	1,4-diamino-anthraquinone,	
	1,4-diamino-2-cyano-anthraquinone,	
25	1,4-diamino-2-methoxy-anthraquinone,	25
	1,4-diamino-2-carbamoyl-anthraquinone,	
	1,4-diamino-5-nitro-anthraquinone,	
	1,4-diamino-2,3-dimethoxy-anthraquinone,	
	1,4-diamino-2,3-dicyano-anthraquinone,	
30	1,4-bis-(para-amino-anilino)-5-hydroxy-anthraquinone,	30
	1,4-bis-(para-amino-anilino)-5,8-dihydroxy-anthraquinone,	
	1,4-bis-(para-amino-anilino)-anthraquinone,	
	1,5-bis-(para-amino-anilino)-2-methyl-anthraquinone,	
	1,5-bis-(para-amino-anilino)-4,8-dihydroxy-anthraquinone	
35	1,5-bis-(para-amino-anilino)-2-(β -hydroxyethylmercapto)-anthraquinone,	35
	1,5-bis-(β -hydroxyethylamino)-anthraquinone,	
	1,4-dihydroxy-2-[β -(β' -hydroxyethyl)- β -hydroxyethyl]-anthraquinone,	
	1,4-dihydroxy-2-[β -(β' -hydroxyethyl)- β -mercaptoethyl]-anthraquinone,	
40	1,4-dihydroxy-2-[β -(β' -hydroxyethyl)- β' -hydroxyethyl]- β -hydroxyethyl]-anthraquinone,	40
	1,6-diamino-anthraquinone,	
	1,8-diamino-anthraquinone,	
	1,8-diamino-2-methyl-anthraquinone,	
45	1-methylamino-2-isopropylmercapto-anthraquinone,	45
	1-methylamino-4-butylamino-anthraquinone,	
	1-anilino-2-chloro-4-amino-anthraquinone,	
	1-methylamino-4-(para-amino-anilino)-anthraquinone,	
	1-methylamino-anthraquinone,	
50	1,4,5-triamino-anthraquinone,	50
	1,4,5-trihydroxy-anthraquinone,	
	1,4,5,8-tetraamino-anthraquinone,	
	1,4,5,8-tetrahydroxy-anthraquinone,	
	1-(amino- or hydroxy)-(4-methoxy, -ethoxy, -propoxy, -isobutoxy- or cyclohexyloxy)-anthraquinone,	
55	1-(amino- or hydroxy)-4- or -5-[2',3'- or 4'-(chloro-, fluoro-, bromo-, methyl-, methoxy-, β -methoxyethyl-, -cyano- or trifluoromethyl)-phenylamino]-anthraquinone,	55
	1-(amino or hydroxy)-4- or -5-[2',3' or 4'-(chloro-, fluoro-, bromo-, methyl-, methoxy- or ethyl)-benzoylamino]-anthraquinone,	
60	1-(amino- or hydroxy)-4- or -5-(methyl-, ethyl-, propyl-, isopropyl-, butyl, isobutyl- or tertiary butyl-, β -methoxyethyl-, β -cyanoethyl- or chloromethyl)-carbonylamino-anthraquinone,	60
	1-(amino- or hydroxy)-4- or -5-(methyl-, ethyl-, propyl-, β -methoxyethyl or β -cyanoethyl)-amino-anthraquinone,	
	1,5-diamino-4,8-dihydroxy-2-(β -hydroxyethylmercapto)-anthraquinone,	
65	1-amino-4-cyclohexylamino-2-anthraquinone carboxamide,	65

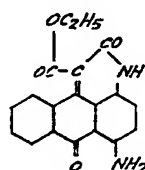
- 1,4-diamino-2,3-anthraquinone dicarboximide,
 1-hydroxy-4-amino-2,3-anthraquinone dicarboximide,
 1,4-diamino-anthraquinone-2,3-dicarboxylic acid- β -hydroxyethylimide,
 and polynuclear anthraquinones consisting of at least 4 nuclei, for example
 4- or 5-amino-1,9-isothiazolanthrone,
 4- or 5-amino-1,9-anthrapyrimidine,
 4- or 5-amino-pyrazolanthrone,
 2- or 3-amino-benzanthrone,
 and the dyestuffs of the formulae

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and



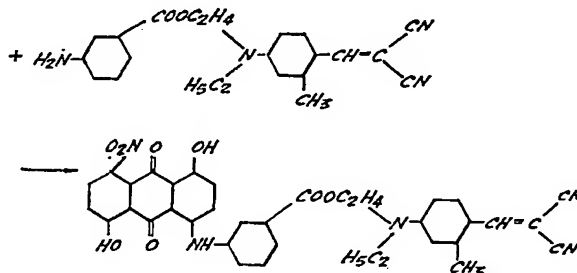
- Compounds belonging to the 2- or 3-phenylanthraquinones substituted in position
 1,4,5,8 are the following:
- 15 1,5 - dihydroxy - 4,8 - diamino - 2- or -3 - (3' - methoxy - 4' - hydroxyphenyl) - anthraquinone, 15
- 1,5 - dihydroxy - 4,8 - diamino - 2- or -3 - (4' - hydroxyphenyl) - anthraquinone,
 1,5 - dihydroxy - 4,8 - diamino - 2- or -3 - (4' - hydroxy - 2' - methylphenyl) - anthraquinone,
- 20 1,5 - dihydroxy - 4,8 - diamino - 2- or -3 - (4' - hydroxyphenyl) - 6- or -7 - bromo - anthraquinone and 20
- 1,5 - dihydroxy - 4,8 - diamino - 2- or -3 - (4' - hydroxy - 3' - or 2' - bromophenyl) - anthraquinone.

- It is preferable to start from anthraquinone derivatives that contain amino groups,
 advantageously only one amino group, as reactive group.

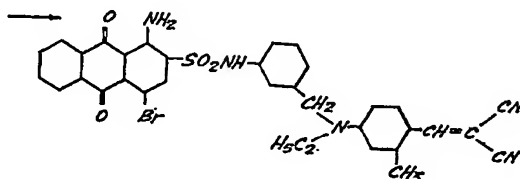
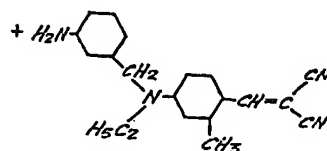
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The reaction can be illustrated by the following typical reaction courses:

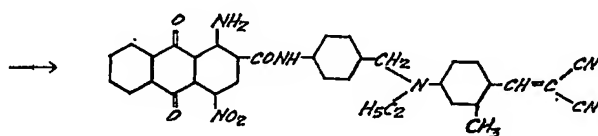
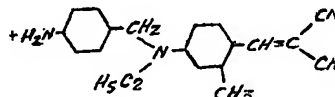
1,5-dihydroxy-4,8-
 dinitro-anthra-
 quinone



1-amino-4-bromo-anthraquinone
2-sulphonic acid chloride

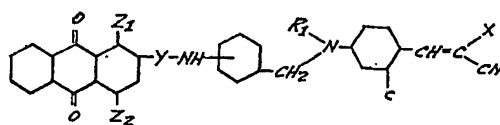


1-amino-2-chlorocarbonyl-
4-nitroanthraquinone



5 By the two last-mentioned reactions there are formed dyestuffs of the general formula

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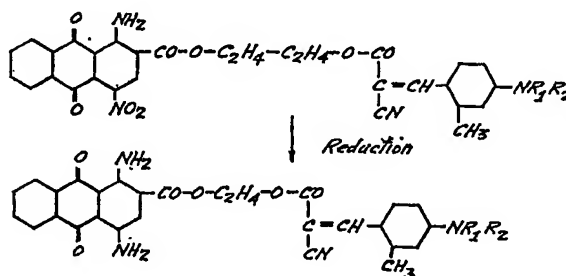
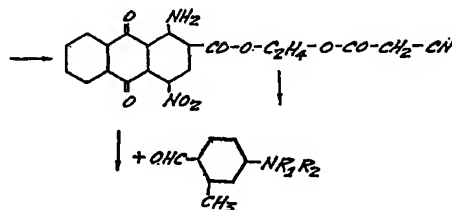


in which Z_1 , Z_2 , Y , R_1 , c and X have the meanings defined above.

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1-amino-2-chlorocarbonyl-4-nitroanthraquinone + $\text{HO}-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{CH}_2-\text{CN}$



in which R_1 and R_2 have the same meanings as above.

In general, the reaction is carried out in an organic solvent, for example, tetrahydrofuran, dimethylglycol ether, dioxan, chlorobenzene, nitrobenzene, dimethylformamide or sulfolan, or in an acid-binding organic medium, for example, pyridine.

Acylation with fibre-reactive acylating agents

5 The anthraquinonoid dyestuffs containing at least one residue of a styryl dyestuff, prepared according to this invention, can subsequently be treated with a fibre-reactive acylating agent provided they contain acylatable groups, especially acylatable amino groups. 5

10 By reaction with the corresponding halides or, if desired, anhydrides there are obtained dyestuffs which are sparingly soluble or insoluble in water, whose molecule contains at least one fibre-reactive group, for example, s-triazinyl residues, which carry on the triazine ring 1 or 2 chlorine or bromine atoms, pyrimidyl residues which carry 1 or 2 chlorine atoms or 1 or 2 arylsulphonyl or alkanesulphonyl groups on the pyrimidine ring, mono- or bis-(γ -halogeno- β -hydroxypropyl)-amino groups, β -halogenethylsulphamyl residues, β -halogenethoxy groups, β -halogenethylmercapto groups, γ -halogeno- β -hydroxypropylsulphamyl residues, chloroacetyl amino groups, vinylsulphonyl groups, 2,3-epoxypropyl groups or other fibre-reactive residues, preferably such as are free from groups imparting solubility in water. 15

(III) *Use*

20 Most of the dyestuffs described above contain no acid groups imparting solubility in water, especially no sulphonic acid groups, so that they are sparingly soluble to insoluble in water. 20

25 The water-insoluble dyestuffs, mixtures of such water-insoluble dyestuffs and their mixtures with other dyestuffs are extremely suitable—especially after having been finely dispersed, for example by grinding, pasting or precipitation—for dyeing or printing synthetic fibres, for example, acrylic or acrylonitrile fibres, polyacrylonitrile fibres and copolymers of acrylonitrile and other vinyl compounds, for example, acrylic esters, acrylamides, vinylpyridine, vinylchloride or vinylidenechloride, copolymers of dicyanoethylene and vinylacetate, also acrylonitrile block copolymers, fibres of polyurethanes, polyolefins, cellulose tri- and 2½-acetate, polyamides, for example, nylon 6, 30 nylon 6.6 or nylon 12, and more especially fibres of aromatic polyesters, for example, of terephthalic acid and ethyleneglycol or 1,4-dimethylolcyclohexane, and copolymers of terephthalic or isophthalic acid and ethyleneglycol. 30

35 Accordingly, the present invention also provides a process for dyeing or printing synthetic fibres, especially polyester fibres, wherein a dyestuff of anthraquinonoid nature, which is free from sulphonic acid groups and contains at least one residue of a styryl dyestuff as above defined, a mixture of such a dyestuff, or a mixture of such a dyestuff with another dyestuff, is used. 35

40 For dyeing, the water-insoluble dyestuffs are advantageously used in a finely dispersed form and dyeing is carried out in the presence of a dispersant, for example, sulphite cellulose waste liquor or of a synthetic detergent, or of a combination of different wetting and dispersing agents. As a rule, it is advantageous to convert the dyestuffs to be used in a dye preparation before dyeing, which preparation contains a dispersant and the finely dispersed dyestuff in such a form that when the dyestuff preparation is diluted with water a fine dispersion results. Such dyestuff preparations can be manufactured by a method known *per se*, for example by grinding the dry or 45 wet dyestuff with or without addition of a dispersant during grinding. It is also possible to dye the afore-mentioned synthetic fibres in a solution of the dyestuff in an organic solvent. 45

50 In aiming at strong dyeings on polyethyleneterephthalate fibres it is advantageous to add a swelling agent to the dyebath, or to carry out the dyeing process under super-atmospheric pressure at a temperature above 100°C, for example at 120°C. Suitable swelling agents are aromatic carboxylic acids, for example benzoic or salicylic acid, phenols, for example ortho- or para-hydroxydiphenyl, salicylic acid methyl ester, aromatic halogen compounds, for example chlorobenzene, ortho-dichlorobenzene or tri- 55 chlorobenzene, phenylmethylcarbinol or diphenyl. For dyeing under super-atmospheric pressure it is advantageous to make the dyebath slightly acidic, for example by adding a weak acid, for example, acetic acid, to it. 55

60 The dyestuffs to be used according to this invention are especially suitable for dyeing by the so-called thermosetting process according to which the fabric to be dyed is impregnated with an aqueous dispersion of the dyestuff, which advantageously contains 1 to 50% of urea and a thickener, especially sodium alginate, preferably at a 60

temperature not exceeding 60°C and then to express it by a method known *per se*.

For fixing the dyestuff on it, the fabric thus impregnated, advantageously after first having been dried, for example in a current of warm air, is heated to a temperature above 100°C, for example a temperature within the range from 180 to 210°C.

The above-mentioned thermosetting process is especially suitable for dyeing union fabrics of polyester fibres and cellulose fibres, especially cotton. In this case the padding liquor contains, in addition to the unquaternated water-insoluble dyestuff to be used according to this invention, also dyestuffs suitable for dyeing cotton, or especially so-called reactive dyestuffs, that is to say dyestuffs than can be fixed on the cellulose fibre with formation of a covalent chemical bond, thus, for example, dyestuffs that contain a chlorotriazine or chlorodiazine residue. In the latter case it has been found advantageous to add an acid acceptor, for example, a carbonate, phosphate, borate or perborate of an alkali metal, or a mixture thereof, to the dye bath. When vat dyestuffs are used, the padded fabric is first heat-treated and then treated with an aqueous alkaline solution of one of the reducing agents conventionally used in vat dyeing.

The dyeings on polyester fibres obtained by the present process are advantageously subjected to an after-treatment, for example, by heating them with an aqueous solution of a nonionic detergent.

The quaternated dyestuffs may be used for dyeing polyacrylic fibres.

The dyestuffs used in the present process may be applied by printing instead of by impregnation. For this purpose, for example, a printing ink is used that contains in addition to the auxiliaries generally used in printing for example, wetting and thickening agents, the finely dispersed dyestuff, if desired in admixture with one of the above-mentioned cotton dyestuffs, if desired in the presence of urea and/or of an acid acceptor.

Furthermore, it is also possible to dye or print in an organic liquor, for example in a mixture of perchloroethylene and sufficient dimethylacetamide to enable the dyestuff to dissolve in the dye liquor.

The new dyestuffs can also be used for spin-dyeing polyamides, polyesters or polyolefins. The polymer to be dyed is advantageously admixed with the dyestuff in the form of a powder, granules or chips, as a ready spinning solution or in the molten state, and the dyestuff is used in the dry state or in the form of a dispersion or solution in a solvent which, if desired, may be volatile.

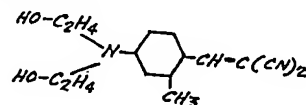
The dyestuffs of the present invention can also be used for mass dyeing polymers of acrylonitrile, or polyolefins and other plastic masses, also for colouring oil paints and lacquers. If desired, the above-mentioned thermosetting process may be applied.

Some of the new dyestuffs are valuable pigments that can be used for a wide variety of pigment applications, for example in the finely dispersed form for dyeing rayon and viscose or cellulose ethers and esters, for the manufacture of inks, especially inks for ballpens, as well as for the manufacture of coloured lacquers or lake formers, solutions and products of acetylcellulose, nitrocellulose, natural or synthetic resins, for example, polymerization or condensation resins, for example aminoplasts, alkyd resins, phenoplasts, polyolefins, for example, polystyrene, polyvinylchloride, polyethylene, polypropylene, polyacrylonitrile, rubber, casein, silicone and silicone resins.

The following Examples illustrate the invention. Unless otherwise indicated, the parts and percentages are by weight.

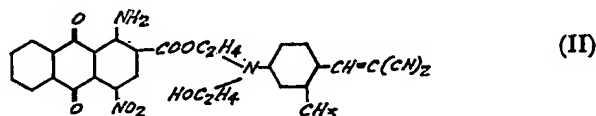
EXAMPLE 1

16.5 Parts of 1-amino-4-nitroanthraquinone-2-carboxylic acid chloride and 13.5 parts of a styryl dyestuff of the formula



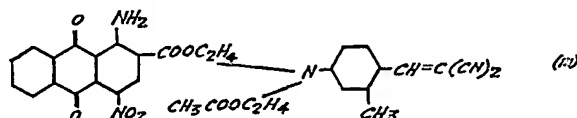
(I)

in chlorobenzene are stirred for 16 hours in an oilbath maintained at 140°C. The cooled mixture is suction-filtered and the filter cake washed with chlorobenzene. The residue is suspended in warm methanol, again suction-filtered and washed with methanol until the filtrate runs colourless. After drying, a product of the formula



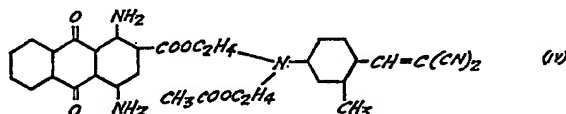
is obtained; this dyestuff dyes polyester fibres yellow shades.

11.3 Parts of the dyestuff of the formula (II) and 40 parts of acetic anhydride are stirred for 2 hours in an oilbath maintained at 140 to 150°C, then poured out over ice, the whole is left to stand for 1 hour and then suction-filtered, thoroughly washed with water and dried, to give an almost quantitative yield of the dyestuff of the formula



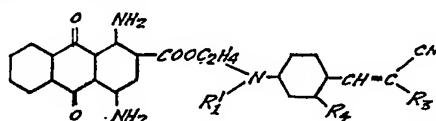
which dyes polyester fibres yellow shades.

The catalytic hydrogenation of the dyestuff of the formula (III) in dimethylformamide in the presence of Raney nickel gives, after the calculated quantity of hydrogen gas has been absorbed, an almost theoretical yield of the dyestuff of the formula



which dyes polyester fibres vivid green shades having good fastness properties.

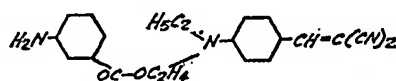
An analogous reaction produces the dyestuffs of the formula



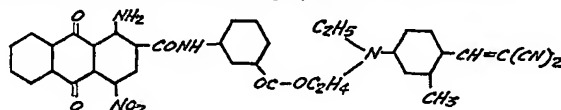
R_1'	R_4	R_3
$-\text{C}_2\text{H}_4\text{CN}$	$-\text{H}$	$-\text{CN}$
$-\text{C}_2\text{H}_4\text{CN}$	$-\text{H}$	$-\text{COOC}_2\text{H}_5$
$-\text{C}_2\text{H}_5$	$-\text{CH}_3$	$-\text{SO}_2-\text{C}_6\text{H}_5$
$-\text{CH}_2-\text{C}_6\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_5$	$-\text{Cl}$	$-\text{CN}$
$-\text{C}_2\text{H}_5$	$-\text{OCH}_3$	$-\text{CONH}_2$
$-\text{C}_2\text{H}_4\text{OCH}_3$	$-\text{H}$	$-\text{CN}$
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{CN}$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{C}_6\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{C}_6\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{Cl}(-p)$	$-\text{CH}_3$	
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{C}_2\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{O}-\text{C}_2\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{NH}-\text{C}_4\text{H}_9$	$-\text{CH}_3$	$-\text{CN}$

EXAMPLE 2

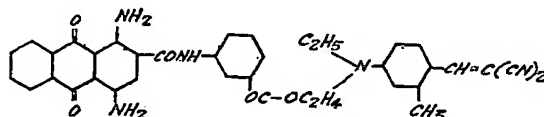
3.3 Parts of 1-amino-4-nitro-anthraquinone-2-carboxylic acid chloride and 3.74 parts of a styryl dyestuff of the formula



- 5 in chlorobenzene are stirred for 16 hours on an oilbath maintained at 140°C. The cooled reaction mixture is suctioned off, washed with chlorobenzene and then with methanol, and dried. 6 Parts of the resulting dyestuff of the formula

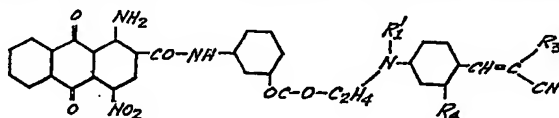


- 10 (which dyes polyester fibres yellow shades) are catalytically hydrogenated in 50 parts of dimethylformamide in the presence of Raney nickel, until the calculated quantity of hydrogen has been absorbed. The resulting dyestuff of the formula



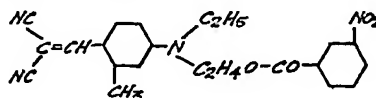
dyes polyester fibres green shades having good fastness properties.

In an analogous manner there are obtained the dyestuffs of the formula

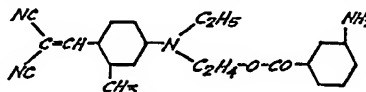


R_1'	R_4	R_3
$-\text{C}_2\text{H}_4\text{CN}$	$-\text{H}$	$-\text{CN}$
$-\text{C}_2\text{H}_4\text{CN}$	$-\text{H}$	$-\text{COOC}_2\text{H}_5$
$-\text{C}_2\text{H}_5$	$-\text{CH}_3$	$-\text{SO}_2-\text{C}_6\text{H}_5$
$-\text{CH}_2\text{C}_6\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_5$	$-\text{Cl}$	$-\text{CN}$
$-\text{C}_2\text{H}_5$	$-\text{OCH}_3$	$-\text{CONH}_2$
$-\text{C}_2\text{H}_4\text{OCH}_3$	$-\text{H}$	$-\text{CN}$
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{CN}$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{C}_6\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{C}_6\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{C}_6\text{H}_4-\text{Cl}(-p)$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{C}_2\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{O}-\text{C}_2\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{NH}-\text{C}_4\text{H}_9$	$-\text{CH}_3$	$-\text{CN}$

Manufacturing the styryl dyestuff
4 Parts of the product of the formula



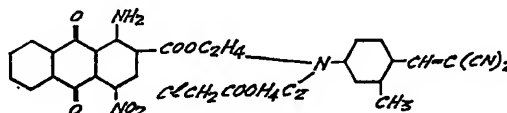
- 5 (prepared by acylating the β -hydroxyethyl compound with meta-nitrobenzoylchloride) in acetonitrile are hydrogenated with a catalyst of 10% palladium on carbon until the quantity of hydrogen needed to reduce the nitro group has been absorbed. No more starting material can be identified in the thin-layer chromatogram. The acetonitrile is distilled off and the residue worked up, to yield the dyestuff of the formula 5



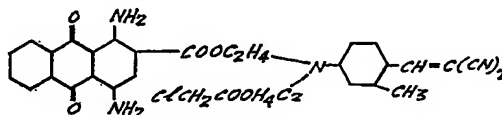
- 10 The para- and ortho-aminobenzoyl esters are obtained in a similar manner. The styryl dyestuffs, in which the N-ethyl group is replaced by a substituted alkyl group, are obtained by using the suitably modified starting compounds. 10

EXAMPLE 3

- 15 5.65 Parts of the product of formula (II) mentioned in Example 1 and 2.26 parts of chloroacetylchloride in nitrobenzene are stirred for 20 hours at 90 to 95°C. After cooling, the batch is suction-filtered, washed with methanol and dried, to yield a product of the formula 15



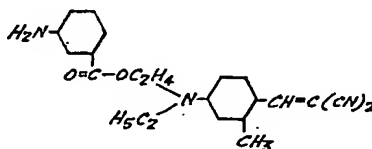
- 20 which dyes polyester fibres yellow shades. The catalytic hydrogenation of 1.9 parts of this product in 25 parts of dimethylformamide with Raney nickel until the theoretical quantity of hydrogen gas has been absorbed gives an almost quantitative yield of a dyestuff of the formula 20



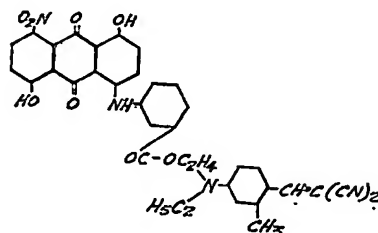
- 25 which dyes polyester and nylon fibres vivid green shades having good fastness properties. 25

EXAMPLE 4

3.5 Parts of 1,5-dihydroxy-4,8-dinitroanthraquinone and 7.5 parts of a styryl dyestuff of the formula



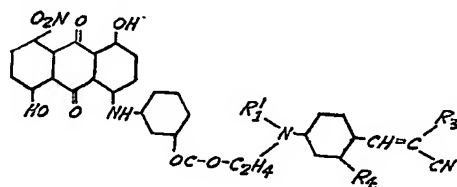
- 30 in nitrobenzene are stirred for 20 hours in a bath maintained at 180°C with a catalytic quantity of copper-(I)-chloride. After cooling, the mixture is poured into methanol. The precipitated dyestuff is suctioned off and the filter cake boiled in methanol, suctioned off, washed with methanol and dried, to yield a dyestuff of the formula 30



which dyes polyester fibres green shades.

When this dyestuff is reduced catalytically with Raney nickel in dimethylformamide until the theoretical quantity of hydrogen has been absorbed, the nitro group is reduced to the amino group and the resulting dyestuff likewise dyes polyester fibres brilliant green shades.

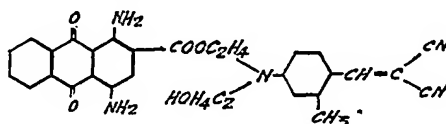
In an analogous manner there are obtained the dyestuffs of the formula



R_1'	R_4	R_3
$-\text{C}_2\text{H}_4\text{CN}$	$-\text{H}$	$-\text{CN}$
$-\text{C}_2\text{H}_4\text{CN}$	$-\text{H}$	$-\text{COOC}_2\text{H}_5$
$-\text{C}_2\text{H}_5$	$-\text{CH}_3$	$-\text{SO}_3-\text{C}_6\text{H}_5$
$-\text{CH}_2\text{C}_6\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_5$	$-\text{Cl}$	$-\text{CN}$
$-\text{C}_2\text{H}_5$	$-\text{OCH}_3$	$-\text{CONH}_2$
$-\text{C}_2\text{H}_4\text{OC}_2\text{H}_4\text{CN}$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{C}_6\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4\text{OCH}_3$	$-\text{H}$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{C}_6\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{C}_2\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{O}-\text{C}_2\text{H}_5$	$-\text{CH}_3$	$-\text{CN}$
$-\text{C}_2\text{H}_4-\text{O}-\text{CO}-\text{NH}-\text{C}_4\text{H}_9$	$-\text{CH}_3$	$-\text{CN}$

EXAMPLE 5

When the product of the formula (II) mentioned in Example 1 is subjected to catalytic reduction with Raney nickel in dimethylformamide, the dyestuff of the formula



5 is obtained; it dyes polyester fibres brilliant green shades having excellent fastness properties.

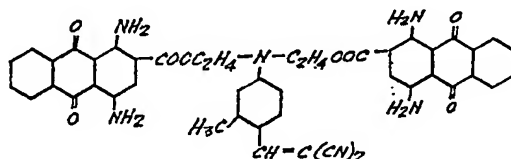
1 Part of the resulting dyestuff is ground wet with 2 parts of an aqueous solution of 50% strength of the sodium salt of dinaphthylmethane-disulphonic acid and then dried.

10 This dyestuff preparation is stirred with 40 parts of an aqueous solution of 10% strength of the sodium salt of N-benzyl-*u*-heptadecyl-benzimidazole-disulphonic acid and 4 parts of 40% acetic acid solution are added. This batch is diluted with water to form a dyebath of 4000 parts.

15 100 Parts of a cleaned polyester fibre fabric are immersed in this dyebath at 50°C, the temperature is raised to 120° to 130°C during half an hour and dyeing is carried out in a closed vessel for 1 hour at this temperature. The material is then thoroughly rinsed. The resulting brilliant green dyeing has excellent properties of fastness to light and sublimation.

EXAMPLE 6

20 When 33 parts of 1-amino-4-nitro-anthraquinone-2-carboxylic acid chloride are reacted with 13.5 parts of the styryl dyestuff of the formula (I) mentioned in Example 1, followed by catalytic reduction as described in Example 1, the dyestuff of the formula



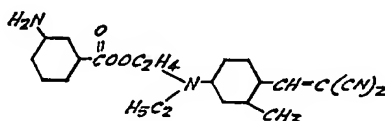
25 is obtained which also dyes polyester fibres fast green shades.

20 Parts of this dyestuff are ground with 140 parts of water containing 40 parts of sodium dinaphthylmethanedisulphonate.

30 A padding liquor is prepared from 200 parts of the above dyestuff preparation, 100 parts of carboxymethylcellulose (4% aqueous solution) and 700 parts of water by stirring the dyestuff preparation described above into the previously diluted thickening by means of a high-speed stirrer, and the mixture is then adjusted to a pH-value of 6 by means of acetic acid of 80% strength. A fabric of polyester fibres is padded in this liquor at 30°C and then expressed to a weight increase of 60%, and then dried at 70 to 80°C. The fabric is then heated on a tenter frame for 60 seconds at 210°C, then washed in hot water and thoroughly rinsed in cold water. A green dyeing of good fastness properties is obtained.

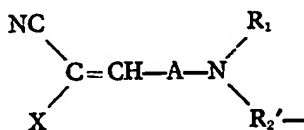
EXAMPLE 7

A mixture of 7.2 parts of 1-amino-4-bromoanthraquinone-2-carboxylic acid chloride and 7.5 parts of the styryl dyestuff of the formula



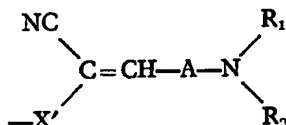
in 50 parts by volume of chlorobenzene is stirred and refluxed for 16 hours, then cooled and the residue is filtered off and washed with benzene. After drying, there are obtained 12.2 parts of the dyestuff of the formula

4. An anthraquinonoid dyestuff as claimed in any one of claims 1 to 3, which contains a styryl residue of the formula



5 in which R_1 represents an unsubstituted or substituted alkyl group, R_2' represents an unsubstituted or substituted alkylene group, A represents an unsubstituted or substituted *p*-phenylene group and X represents a negative substituent as herein defined. 5

5. An anthraquinonoid dyestuff as claimed in any one of claims 1 to 3, which contains a residue of the formula



10 in which A represents an unsubstituted or substituted *p*-phenylene group, R_1 and R_2 each represents an unsubstituted or substituted alkyl group and may be the same or different, and X' represents a residue bound to the residue of the styryl dyestuff through an $-\text{SO}_2-$ or $-\text{CO}-$ bridge. 10

15 6. An anthraquinonoid dyestuff as claimed in claim 5, wherein X' represents an $-\text{SO}_2-$ arylene, $-\text{SO}_2-\text{N}-(\text{alkyl})-\text{alkylene}$, $-\text{CO}-\text{N}-(\text{alkyl})-\text{alkylene}$ or $-\text{CO}-\text{O}-\text{alkylene}$ residue, in which alkyl and alkylene represent unsubstituted or substituted alkyl, aralkyl or cycloalkyl groups. 15

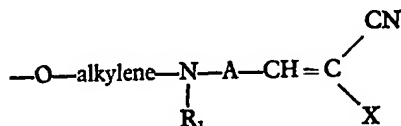
7. An anthraquinonoid dyestuff as claimed in claim 4, which contains a styryl residue of the formula



20

in which R represents a hydrogen atom or an alkyl group containing 1 to 4 carbon atoms, and R_1 , X and A have the same meanings given in claim 6. 20

8. An anthraquinonoid dyestuff as claimed in claim 4, which contains a styryl residue of the formula



25

in which R_1 , X and A have the same meanings as in claim 4. 25

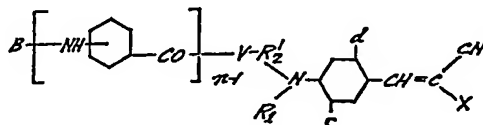
9. An anthraquinonoid dyestuff as claimed in any one of claims 1 to 6, wherein the styryl dyestuff is bound to the α -position in the anthraquinone residue. 30

10. An anthraquinonoid dyestuff as claimed in any one of claims 1 to 6, wherein the styryl dyestuff is bound to the β -position in the anthraquinone residue. 30

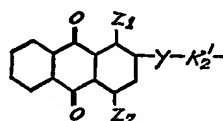
11. An anthraquinonoid dyestuff as claimed in any one of claims 1 to 6, which is a polynuclear anthraquinone consisting of at least 4 nuclei. 35

12. An anthraquinonoid dyestuff as claimed in any one of claims 1 to 6, which contains either two anthraquinone residues or two styryl residues. 35

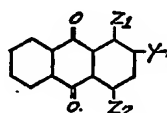
13. An anthraquinonoid dyestuff as claimed in claim 4, which corresponds to the formula



in which V represents —O— or —NH—, R₁ represents an unsubstituted or substituted alkyl group or a residue of the formula



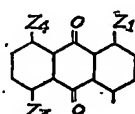
5 in which R₂' represents an unsubstituted or substituted alkylene group, Y represents an —SO_n— or a —CO— group, n=1 or 2, c and d each represents a hydrogen or chlorine atom or a methyl, ethyl, methoxy, ethoxy, phenylthio or phenoxy group, X represents a carbalkoxy group, a carbonamido group, an arylsulphonyl or a cyano group, B represents a residue of the formula



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or

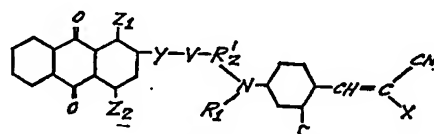
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15 in which Z₁ represents an amino group which may be alkylated or a hydroxyl group, Z₂ represents an amino group which may be alkylated or a nitro group or a bromine atom, and Z₃ and Z₄ each represents a nitro or hydroxyl group or an amino group which may be alkylated.

15

14. An anthraquinonoid dyestuff as claimed in claim 13, which corresponds to the formula

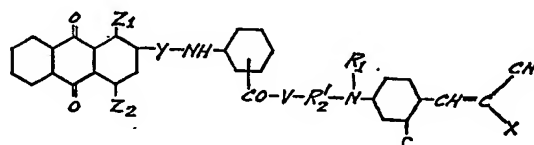


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in which Z₁, Z₂, Y, V, R₁, R₂', c and X have the meanings given in claim 13.

15. An anthraquinonoid dyestuff as claimed in claim 13, which corresponds to the formula

20

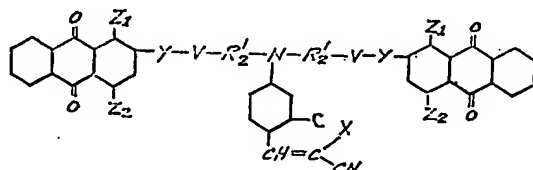


in which Z₁, Z₂, Y, V, R₁, R₂', c and X have the meanings given in claim 13.

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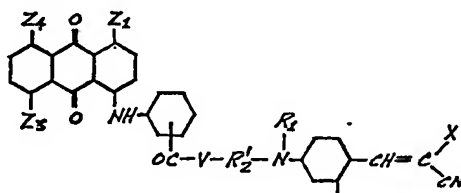
16. An anthraquinonoid dyestuff as claimed in claim 13, which corresponds to the formula

25



in which Z₁, Z₂, Y, V, R₂', c and X have the meanings given in claim 13.

17. An anthraquinonoid dyestuff as claimed in claim 13, which corresponds to the formula



in which Z_1 , Z_2 , Z_3 , V , R_1 , R_2' , c and X have the meanings given in claim 15.

18. An anthraquinonoid dyestuff as claimed in claim 14 or 15, wherein Y represents a carbonyl residue and V represents an oxygen atom.

19. An anthraquinonoid dyestuff as claimed in claim 17, wherein V represents an oxygen atom.

20. Any one of the anthraquinone dyestuffs as claimed in claim 1, substantially as described in any one of the Examples herein.

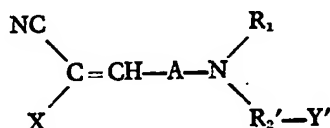
21. A process for the manufacture of dyestuffs of the anthraquinone series free from sulphonic acid groups, wherein at least one anthraquinone derivative is condensed according to known methods with at least one styryl dyestuff containing a styryl radical of the formula $>C=CH-1,4\text{-arylene}-N<$ in which the terminal carbon atoms carries two organic residues, and the resulting anthraquinone-styryl dyestuff, if desired, is acylated according to known methods with a fibre-reactive group containing acylating agent as herein defined.

22. A process as claimed in claim 21, wherein both starting dyestuffs are disperse dyestuffs.

23. A process as claimed in claim 21 or 22, wherein one of the starting dyestuffs contains at least one labile hydroxyl or amino group.

24. A process as claimed in claim 23, wherein the starting styryl dyestuff contains a hydroxyl or an amino group.

25. A process as claimed in claim 24, wherein a starting styryl dyestuff of the formula



is used, in which R_1 represents an unsubstituted or substituted alkyl group, R_2' represents an unsubstituted or substituted alkylene group, A represents an unsubstituted or substituted p -phenylene group, X represents a negative substituent and Y' represents a group which contains a labile hydroxyl or amino group.

26. A process as claimed in claim 25, wherein Y' represents a hydroxyl or an aminobenzoyloxy residue.

27. A process as claimed in claim 23, wherein an anthraquinonoid starting dyestuff is used which contains in β -position a carboxylic acid halide or sulphonic acid halide group.

28. A process as claimed in claim 23, wherein an α -nitro group in an α -nitro-anthraquinone is replaced by the amino group of an aminostyryl dyestuff.

29. A process as claimed in any one of claims 21 to 28, wherein the reaction is carried out in an organic solvent.

30. A process as claimed in claim 29, wherein the organic solvent is tetrahydrofuran, dimethylglycol ether, dioxan, chlorobenzene, nitrobenzene, dimethylformamide or sulpholan.

31. A process as claimed in any one of claims 21 to 30, wherein the reaction is carried out in an acid-binding organic medium.

32. A process as claimed in claim 31, wherein the acid binding organic medium is pyridine.

33. A process for dyeing or printing synthetic fibres, wherein a dyestuff claimed in any one of claims 1 to 20 is used.

34. A process as claimed in claim 33, wherein polyester or nylon fibres are dyed or printed.

35. Material dyed by a process claimed in claim 33 or 34.

36. A process for pigmenting high-molecular organic material, wherein a water-insoluble dyestuff as claimed in any one of claims 1 to 20 is used.
37. A process for dyeing synthetic fibre-forming polymers, in the spinning solution, using a dyestuff as claimed in any one of claims 1 to 20.
- 5 38. A process as claimed in claim 37, wherein the polymer is of a polyester, polyolefin or a polyamide. 5
39. Material dyed by a process claimed in claim 37 or 38.
40. A process for dyeing polyacrylic fibres, wherein a quaternated dyestuff as claimed in any one of claims 1 to 20 is used.
- 10 41. Material dyed by a process claimed in claim 40. 10

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Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1972.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.